

DESCRIPTION

ANTIFOULING COATING COMPOSITION

Technical Field

[0001]

The present invention relates to an antifouling coating composition.

Background Art

[0002]

Aquatic fouling organisms such as barnacles, tubeworms, common mussels, *Bugula neritina*, sea squirts, green laver, sea lettuce, and slimes adhere to ships (especially ship bottoms), fishing tools such as fishing nets and fishing net accessories, and structures submerged in seawater such as power plant aqueducts, leading to dysfunction, impaired appearance, and other problems of the ships and the like.

In order to prevent such problems, a technique which forms an antifouling coating film by coating an antifouling coating composition on a ship and the like, and allows controlled release of an antifouling agent to realize an antifouling performance for a long time has been known (Patent Literature 1).

Citation List

Patent Literature

[0003]

[Patent Literature 1] JP-A-2000-17203

Summary of Invention

Technical Problem

[0004]

Although by adopting the technique of Patent Document 1, a certain degree of a coating film dissolution speed is secured in a sea area having a normal temperature to a high temperature, the coating film dissolution speed extremely reduces in a sea area having a low temperature, and especially the antifouling performance at the initial stage is not sufficient. Further, after immersion in seawater, coating film defects such as cracks may occur in a relatively short period of time, and further improvement is required.

[0005]

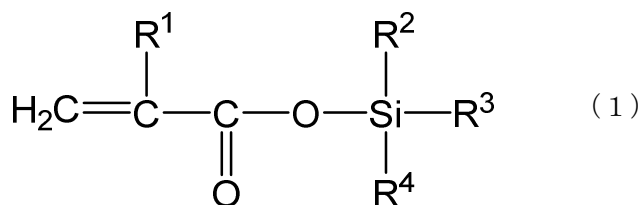
The present invention has been made by taking the afore-mentioned circumstances into consideration. The present invention provides an antifouling coating composition which can maintain a stable coating film dissolution rate for a long period of time in a low temperature sea area and stable antifouling performance without causing coating film defects such as cracks.

Solution to Problem

[0006]

According to the present invention, an antifouling coating composition, comprising: a copolymer A; a polymer B; and a plasticizer C; wherein: the copolymer A is a copolymer of a monomer (a) and an ethylenically unsaturated monomer (b) other than the monomer (a); the monomer (a) is represented by general formula (1);

[chemical formula 1]



in the general formula, R^1 is a methyl group, and R^2 to R^4 are the same or different and each represents a C3-C8 branched alkyl group or a phenyl group; content of the monomer (a) is 15 to 35mass% with respect to a total mass of the monomer (a) and the monomer (b); the polymer B is a (meth)acrylate ester polymer other than the copolymer A and has a weight average molecular weight of 20,000 to 100,000; is provided.

[0007]

The present inventors have conducted intensive studies and have found that a composition comprising a copolymer A, a polymer B, and a plasticizer C can solve the above problem, thereby completing the present invention.

Description of Embodiments

[0008]

Hereinafter, the present invention will be described in detail.

[0009]

1. Antifouling coating composition

An antifouling coating composition of the present invention includes a copolymer A, a polymer B, and a plasticizer C.

[0010]

1-1. Copolymer A

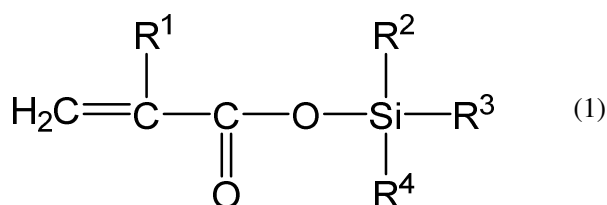
A copolymer A is a copolymer of a monomer (a) and an ethylenically unsaturated monomer (b) other than monomer (a). The copolymer A includes monomeric units derived from monomers (a) to (b).

[0011]

<Monomer (a)>

The monomer (a) is a triorganosilyl methacrylate monomer and is represented by the general formula (1).

[chemical formula 1]



In the general formula, R^1 is a methyl group, and R^2 to R^4 are the same or different and each represents a C3-C8 branched alkyl group or a phenyl group.

[0012]

The C3-C8 branched alkyl group in R^2 to R^4 include, for example, isopropyl group, isobutyl group, s-butyl group, t-butyl group, 1-ethylpropyl group, 1-methylbutyl group, 1-methylpentyl group, 1,1-dimethylpropyl

group, 1,1-dimethylbutyl group, texyl group, cyclohexyl group, 1,1-dimethylpentyl group, 1-methylhexyl group, 1,1-dimethylhexyl group, 1-methylheptyl group, 2-methylbutyl group, 2-ethylbutyl group, 2,2-dimethylpropyl group, cyclohexylmethyl group, 2-ethylhexyl group, 2-propylpentyl group, 3-methylpentyl group and the like. As R^2 to R^4 , isopropyl group, s-butyl group, t-butyl group, phenyl group, and 2-ethylhexyl group are preferable. isopropyl group and 2-ethylhexyl group are particularly preferable.

[0013]

Examples of the monomer (a) include triisopropylsilyl methacrylate, triisobutylsilyl methacrylate, tri-s-butylsilyl methacrylate, triisopentylsilyl methacrylate, triphenylsilyl methacrylate, diisopropyl phenylsilyl methacrylate, diisopropyl isobutylsilyl methacrylate, diisopropyl s-butylsilyl methacrylate, diisopropyl isopentylsilyl methacrylate, isopropyl diisobutylsilyl methacrylate, isopropyl di-s-butylsilyl methacrylate, t-butyl diisopentylsilyl methacrylate, t-butyl diisopentylsilyl methacrylate, t-butyl diphenylsilyl methacrylate, diisopropyl texylsilyl methacrylate, diisopropyl cyclohexylsilyl methacrylate, tricyclohexylsilyl methacrylate, tri-1,1-dimethylpentylsilyl methacrylate, tri-2,2-dimethylpropylsilyl methacrylate, tricyclohexylmethylsilyl methacrylate, diisopropyl cyclohexylmethylsilyl methacrylate, tri-2-ethylhexylsilyl methacrylate, and tri-2-propylpentylsilyl methacrylate. Preferred are triisopropylsilyl methacrylate, tri-s-butylsilyl methacrylate, t-butyl diphenylsilyl methacrylate, tri-2-ethylhexylsilyl methacrylate and the like. These monomers (a) can be used alone or in combination of two or more of these can be used in combination.

[0014]

<Monomer(b)>

The monomer (b) is an ethylenically unsaturated monomer other than monomer (a), and examples thereof include (meth)acrylate ester, vinyl compounds, aromatic compounds, dialkyl ester compounds of dibasic acid, and the like. In this specification, (meth)acrylate ester means an acrylate ester or a methacrylate ester.

[0015]

Examples of the (meth) acrylate ester include methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 2-methoxypropyl (meth)acrylate, 4-methoxybutyl (meth)acrylate, benzyl (meth)acrylate, phenyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, 2-(2-ethoxyethoxy)ethyl (meth)acrylate, propylene glycol monomethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, glycidyl (meth)acrylate, furfuryl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, benzyl (meth)acrylate, and phenyl (meth)acrylate.

[0016]

Examples of the vinyl compounds include vinyl compounds having a functional group such as vinyl chloride, vinylidene chloride, acrylonitrile, methacrylonitrile, vinyl acetate, vinyl benzoate, vinyl butyrate, butyl vinyl ether, lauryl vinyl ether and N-vinylpyrrolidone.

[0017]

The aromatic compounds include, for example, styrene, vinyl toluene, and α -methylstyrene.

[0018]

Dialkyl ester compounds of dibasic acid include dimethyl maleate, dibutyl maleate, and dimethyl fumarate.

[0019]

In the present invention, these monomers (b) may be used alone or in combination of two or more of these can be used in combination. Particularly from the viewpoint of physical properties of the coating film, a monomer (b) is preferably a (meth)acrylate ester, and particularly from the viewpoint of crack resistance, a monomer (b) is more preferably methyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, 2-(2-ethoxyethoxy)ethyl acrylate, 2-hydroxyethyl (meth)acrylate, glycidyl (meth)acrylate, furfuryl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, and the like.

[0020]

The copolymer A is obtained by copolymerizing 15 to 35mass% of the monomer (a) and 65 to 85mass% of the monomer (b), preferably by copolymerizing 20 to 35mass% of the monomer (a) and the monomer (b), more preferably by copolymerizing 25 to 35mass% of the monomer (a) and the monomer (b). The content of the monomer (a) is specifically, for example, 15, 20, 25, 30, 35mass% and may be in the range between any two of the numerical values exemplified herein.

[0021]

In addition, the monomer (b) may contain a silyl ester other than the monomer (a) (a silyl acrylate ester, a silyl methacrylate ester other than the general formula (1)). In that case, the content of the total silyl ester is, for example, 15 to 50mass% with respect to the total mass of the monomer (a) and the monomer (b), and specifically, for example, 15, 20, 25, 30, 35, 40, 45, 50mass%, and may be in a range between any two of the numerical values exemplified herein. The content of the silyl ester other than the monomer (a) is preferably less than the content of the monomer (a) and preferably 1/2 or less of the content of the monomer (a) and more preferably 1/5 of the content of the monomer (a).

[0022]

When the copolymer A within the above range is used as the coating composition of the present invention, film dissolution is improved particularly in low temperature sea areas.

[0023]

The weight average molecular weight (Mw) of the copolymer A is preferably 5,000 to 300,000. When the molecular weight is less than 5,000, the coating film of the antifouling coating becomes fragile and easily peels off or cracks, and when it exceeds 300,000, the viscosity of the copolymer solution increases, and the handling becomes difficult. This Mw may be specifically, for example, 5000, 10000, 20000, 30,000, 40,000, 50,000, 60,000, 70,000, 80,000, 90,000, 100,000, 200,000, 300,000, and may be in the range between the two values exemplified herein.

[0024]

Examples of the method for measuring Mw include gel permeation chromatography (GPC method).

[0025]

The copolymer A may be a random copolymer, an alternating copolymer, a periodic copolymer, or a block copolymer of the monomer (a) and the monomer (b).

[0026]

The copolymer A can be obtained, for example, by polymerizing the monomer (a) and the monomer (b)

in the presence of a polymerization initiator.

[0027]

Examples of the polymerization initiator used in the above polymerization reaction include azo compounds such as 2,2'-azobisisobutyronitrile (AIBN), 2,2'-azobis-2-methylbutyronitrile and dimethyl-2,2'-azobisisobutyrate; and peroxides such as dibenzoyl peroxide, m-toluoyl peroxide, benzoyl m-methylbenzoyl peroxide, di-tert-butyl peroxide, tert-butyl peroxybenzoate, tert-butyl peroxyisopropyl carbonate, tert-butyl peroctoate, tert-butyl peroxy 2-ethylhexanoate, 1,1,3,3-tetramethylbutylperoxy-2-ethylhexanoate, 1,1,3,3-tetramethylbutylperoxyneodecanoate. These polymerization initiators can be used alone or in combination of two or more of these can be used in combination. As the polymerization initiator, AIBN, dibenzoyl peroxide, m-toluoyl peroxide, benzoyl m-methylbenzoyl peroxide, tert-butyl peroctoate, and 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate is preferred.

By suitably controlling the amount of the polymerization initiator being used, the molecular weight of the copolymer A can be adjusted

[0028]

As the method of polymerization, solution polymerization, bulk polymerization, emulsion polymerization, suspension polymerization, non-aqueous dispersion polymerization and the like can be mentioned. Among these, in view of the capability of obtaining the copolymer A simply with accuracy, solution polymerization and non-aqueous dispersion polymerization are preferable.

[0029]

In the polymerization reaction, an organic solvent can be used if necessary. As the organic solvent, for example, aromatic hydrocarbon solvents such as xylene and toluene; aliphatic hydrocarbon solvents such as hexane, heptane, octane, and mineral spirits; ester solvents such as ethyl acetate, butyl acetate, isobutyl acetate, and methoxypropyl acetate; alcohol solvents such as isopropyl alcohol, butyl alcohol, and propylene glycol monomethyl ether; ether solvents such as dioxane, diethyl ether, and dibutyl ether; ketone solvents such as methyl ethyl ketone and methyl isobutyl ketone; and the like can be mentioned. Among these, in particular, aliphatic hydrocarbon solvents, ester solvents, alcohol solvents, aromatic hydrocarbon solvents are preferable, and mineral spirit, butyl acetate, isobutyl acetate, butyl alcohol, propylene glycol monomethyl ether, toluene, xylene are more preferable. These solvents may be used alone or two or more of these can be used in combination.

[0030]

The reaction temperature in the polymerization reaction may be suitably controlled depending on the type of the polymerization initiator used and the like. The reaction temperature is usually 70 to 140°C, preferably 80 to 130°C.

[0031]

The polymerization reaction is preferably performed in an inert gas atmosphere such as nitrogen gas or argon gas.

[0032]

1-2. Polymer B

The polymer B is a (meth)acrylate ester polymer other than the copolymer A and has a weight average molecular weight (Mw) of 20000 to 100000 (GPC method).

[0033]

The polymer B may be a homopolymer of one kind of monomer, but is preferably a copolymer of plural kinds of monomers. The monomer forming the polymer B includes (meth)acrylate ester such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 2-methoxypropyl (meth)acrylate, 4-methoxybutyl (meth)acrylate, benzyl (meth)acrylate, phenyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, 2-(2-ethoxyethoxy)ethyl (meth)acrylate, propylene glycol monomethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, glycidyl (meth)acrylate, furfuryl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, benzyl (meth)acrylate, and phenyl (meth)acrylate and the like.

[0034]

Among them, particularly from the viewpoint of the dissolving property, 2-methoxyethyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, 2-(2-ethoxyethoxy)ethyl acrylate, 2-hydroxyethyl (meth)acrylate, glycidyl (meth)acrylate, furfuryl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate and the like, which contain a hydrophilic functional group such as an alkoxy group and an epoxy group having an ether bond, are preferable.

[0035]

Other monomers which can be polymerized with the above monomers include vinyl compounds such as vinyl chloride, vinylidene chloride, acrylonitrile, methacrylonitrile, vinyl acetate, vinyl benzoate, vinyl butyrate, butyl vinyl ether; lauryl vinyl ether and N-vinylpyrrolidone, and the like; aromatic compounds such as styrene, vinyltoluene, α -methylstyrene, and the like; dialkyl ester compounds of dibasic acid such as dimethyl maleate, dibutyl maleate, dimethyl fumarate, and the like; other ethylenically unsaturated compounds such as ethylene, allyl alcohol, allyl glycidyl ether, (meth) acrylic acid, and the like. From the viewpoint of production cost and availability of raw materials, styrene, vinyl acetate, (meth) acrylic acid, and the like are preferable.

[0036]

As the polymerization method, the initiator, the solvent, the temperature, other conditions, the Mw measurement method, and the like, the method described above for the copolymer A can be applied.

[0037]

The weight average molecular weight of the polymer B is 20,000 to 100,000 (GPC method), preferably 20,000 to 60,000 (GPC method), and more preferably 20,000 to 50,000 (GPC method). This Mw is, specifically, for example, 20,000, 30,000, 40,000, 50,000, 60,000, 70,000, 80,000, 90,000, and 100,000, and may be in the range between any two of the numerical values exemplified herein.

[0038]

The weight average molecular weight of the polymer B can be adjusted by appropriately setting the kind and amount of the initiator and the reaction temperature as described above for the copolymer A.

[0039]

When the polymer B within the above range is used with the copolymer A and the plasticizer, the crack resistance and the adhesion are excellent especially in low temperature sea areas.

[0040]

The content of the polymer B in the composition of the present invention is not particularly limited, but

the content ratio of the copolymer A to the polymer B (the copolymer A/the polymer B) is usually 0.01 to 15, preferably 0.05 to 10, and more preferably 0.1 to 5 by mass ratio in terms of solid content. When the contents of the copolymer A and the polymer B are within the above ranges, the effect of improving crack resistance and film dissolution of the coating composition of the present invention in low temperature sea areas is significantly realized and thereby allowing for providing the coating film which demonstrates a stable film dissolution property for a long period of time without causing coating film defects.

[0041]

1-3. Plasticizer C

As the plasticizer C, for example,

chlorinated paraffin,

vegetable oil plasticizers such as linseed oil, epoxidized linseed oil, soybean oil, and epoxidized soybean oil;

aromatic diester plasticizers such as di-n-octyl phthalate, di-2-ethylhexyl phthalate, isononyl phthalate, diisodecyl phthalate, diisononyl 2,5-furandicarboxylate, diethyl isophthalate, di-2-ethylhexyl isophthalate, diethyl terephthalate, di-2-ethylhexyl terephthalate;

aromatic triester plasticizers such as tributyl trimellitate and tri-2-ethylhexyl trimellitate;

aromatic tetraester plasticizers such as tetra-2-ethylhexyl pyromellitic acid;

alicyclic ester plastics such as 4-cyclohexene-1,2-dicarboxylic acid di-2-ethylhexyl, 1,2-cyclohexanedicarboxylic acid diisononyl, 1,3-cyclohexanedicarboxylic acid diisononyl, 1,4-cyclohexanedicarboxylic acid diisononyl, 4,5-epoxycyclohexane-1,2-dicarboxylic acid di-2-ethylhexyl, 4,5-epoxycyclohexane-1,2-dicarboxylic acid distearyl, and 4,5-epoxycyclohexane-1,2-dicarboxylic acid diepoxystearyl;

fatty acid ester plasticizers such as di-2-ethylhexyl succinate, di-2-butoxyethyl adipate, diisononyl adipate, di-2-ethylhexyl azelate, and di-2-ethylhexyl sebacate;

hydroxycarboxylic acid ester plasticizers such as tributyl citrate, acetyl triethyl citrate, and acetyl tri-2-ethylhexyl citrate;

polyhydric alcohol ether/ester plasticizers such as diethylene glycol dibutyl ether, triethylene glycol diacetate, diethylene glycol dibenzoate, triethylene glycol di(2-ethylhexanoate), propylene glycol dilaurate, monoolein, triacetin, tributyrin;

monoester plasticizers such as decyl decanoate, geranyl acetate, isopropyl myristate, isopropyl palmitate, benzyl isovalerate, benzyl acetoacetate, p-tolyl n-octanoate, benzyl 7,8-epoxystearate, octyl 9,10-epoxystearate, cetyl stearate, isoamyl phenylacetate, 2-ethylhexyl benzoate, hexyl 4-hydroxybenzoate, 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate, 3,7-dimethyl-6-octen-1-olacetate, terpinyl acetate, 4-tert-butylcyclohexyl acetate, menthyl acetate, isobornyl acetate, isobornyl ethylate, isobornyl stearate, methyl dihydrojasmonate, 3,4-epoxycyclohexanecarboxylic acid 3, 4-epoxycyclohexylmethyl, furfuryl acetate, tetrahydrofurfuryl acetate, ethyl 2-furancarboxylate, tetrahydrofurfuryl propionate, n-octyl 2-furan carboxylate, isoamyl 2-furan carboxylate;

phosphate ester plasticizers such as trimethyl phosphate and tricresyl phosphate;

polyvinyl alkyl ether type plasticizers such as Lutonal M40 and Lutonal A25;

polyester plasticizer;

camphor, terpene phenol, t-nonyl pentasulfide and the like;

can be mentioned. These may be used alone, or two or more of these can be used in combination.

[0042]

Among these, from the viewpoint of easy availability, chlorinated paraffin, vegetable oil plasticizers, aliphatic ester plasticizers, aromatic ester plasticizers are preferable, and particularly from the viewpoint of crack resistance in low temperature seawater, chlorinated paraffin, epoxidized soybean oil, diisononyl phthalate, diisononyl 1,2-cyclohexanedicarboxylate, di2-ethylhexyl terephthalate, and tri-2-ethylhexyl trimellitate are more preferable, and from the viewpoint of cost, chlorinated paraffin is more preferable.

[0043]

The content of the plasticizer in the composition of the present invention is not particularly limited, but is usually 0.01 to 30mass% in terms of solid content, and from the viewpoint of the viscosity of the coating and the hardness of the coating film, it is preferably 0.05 to 25mass% and more preferably 0.1 to 20mass%.

[0044]

1-4. Antifouling agent

As the antifouling agent, for example, an inorganic chemical and an organic chemical can be mentioned.

As the inorganic chemical, for example, cuprous oxide, cuprous thiocyanate (generic name: rhodan copper), copper powder, and the like can be mentioned. Among these, cuprous oxide and rhodan copper are particularly preferable. From the viewpoint of long-term shelf stability, the cuprous oxide surface-treated with glycerin, sucrose, stearate, laurate, lecithin, mineral oil, and the like is more preferable.

As the organic chemical, for example, copper 2-mercaptopyridine-N-oxide (generic name: copper pyrithione), zinc 2-mercaptopyridine-N-oxide (generic name: zinc pyrithione), zinc ethylenebis(dithiocarbamate) (generic name: zineb), 4,5-dichloro-2-n-octyl-3-isothiazolone (generic name: Sea-nine 211), 3,4-dichlorophenyl-N,N-dimethylurea (generic name: Diuron), 2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine (generic name: Irgarol 1051), 2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethyl pyrrole (generic name: ECONEA 28), 4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole (generic name: Medetomidine) can be mentioned.

These antifouling agents can be used alone, or two or more of these can be used in combination.

[0045]

1-5. Other additives

Further, if necessary, the resin for antifouling coating of the present invention is added with a copolymer and a resin component other than the copolymer A and the polymer B, an elution regulator, a pigment, a dye, an antifoaming agent, a dehydrating agent, a thixotropic agent, an organic solvent, and the like to obtain the antifouling coating.

[0046]

As the copolymer and the resin component other than the copolymer A and the polymer B, for example, (meth)acrylate resins other than the copolymer A and the polymer B, polyester resins, vinyl resins, petroleum resins, metal-containing resins, resins containing a zwitterionic compound, silicone resins, and the like can be mentioned.

As the elution regulator, monocarboxylic acids and salts thereof, such as rosin, rosin derivatives, naphthenic acid, cycloalkenyl carboxylic acid, bicycloalkenyl carboxylic acid, versatic acid, trimethyl isobutenylcyclohexene carboxylic acid, and their metal salts, or the alicyclic hydrocarbon resins as mentioned above can be exemplified. These can be used alone, or two or more of these can be used in combination.

As the rosin derivatives, hydrogenated rosin, disproportionated rosin, maleic acid modified rosin, formylated rosin, polymerized rosin and the like can be exemplified.

As the alicyclic hydrocarbon resins, Quintone 1500, Quintone 1525L, and Quintone 1700 (product name, available from Zeon Corporation) and the like can be mentioned as commercially available products for example.

Among these, rosin, rosin derivative, naphthenic acid, versatic acid, trimethyl isobutenylcyclohexene carboxylic acid, and metal salts thereof are preferable.

As the dehydrating agent, synthetic zeolite adsorbents, orthoesters, silicates such as tetramethoxysilane and tetraethoxysilane, isocyanates, carbodiimides, carbodiimidazoles, and the like can be mentioned. These can be used alone, or two or more of these can be used in combination.

[0047]

2. Method for producing antifouling coating composition

The antifouling coating composition of the present invention can be manufactured, for example, by mixing and dispersing a mixed solution containing the copolymer A, the polymer B, the plasticizer C, other additives, and the like using a disperser.

Regarding the mixture solution, the ingredients such as the copolymer, the antifouling agent, and the like are preferably dissolved or dispersed in the solvent.

As the disperser, for example, the one which can be used as a micro-pulverizer can be suitably used. For example, a commercially available homo mixer, sand mill, bead mill, and the like can be used. Furthermore, the mixed solution can be mixed and dispersed by using a stirrer-equipped container containing glass beads for mixing and dispersing.

[0048]

3. Method for antifouling treatment, antifouling coating film, and coated object

The method for antifouling treatment of the present invention is characterized in that an antifouling coating film is formed using the above-explained antifouling coating composition on the surface of an object that is subjected to coating. The method for antifouling treatment of the present invention can prevent adhesion of aquatic fouling organisms by the gradual dissolution of the surface of the antifouling coating film such that the surface of the coating film is continually renewed.

Examples of objects on which the coating film can be formed include ships (in particular, ship bottoms), fishing tools, structures submerged in seawater, and the like.

The thickness of the antifouling coating film can be suitably selected depending on the type of the object on which the coating film is to be formed, the navigation speed of a ship, the seawater temperature, and the like. For example, when the object on which a coating film is formed is a ship bottom, the thickness of the antifouling coating film is usually 50 to 700 μm , and preferably 100 to 600 μm .

EXAMPLES

[0049]

Examples and the like are provided hereinafter, and further clarifies characteristics of the present invention. The present invention, however, is not limited to these Examples.

In each of Production Examples, Examples, and Comparative Examples, "%" denotes "% by mass". The viscosity was measured at 25°C using a Brookfield viscometer. The weight average molecular weight (Mw) was determined by gel permeation chromatography (GPC) (using a polystyrene standard). GPC was performed under the following conditions.

Equipment: HLC-8220 GPC (available from Tosoh Corporation)

Column: TSK-gel Super HZM-M, two columns used

Flow rate: 0.35 mL/min

Detector: RI

Column thermostat temperature: 40°C

Developing solvent: THF

The non-volatile content is a value determined in accordance with JIS K 5601-1-2:1999 (ISO 3251:1993) "Testing methods for paint components- Determination of non-volatile matter content".

[0050]

<Production Examples of copolymer solution>

<Production Example 1 (Production of a solution of copolymer A _A-1)>

To a flask equipped with a thermometer, reflux condenser, stirrer, and dropping funnel, 260 g of xylene was charged. While stirring at $85\pm5^{\circ}\text{C}^{\circ}$ under nitrogen atmosphere, a mixed solution of 175 g of triisopropylsilyl methacrylate, 175 g of methyl methacrylate, 25 g of n-butyl acrylate, 25 g of isobutyl methacrylate, 75 g of 2-methoxyethyl acrylate, 25g of 2-methoxyethyl methacrylate, and 3 g of 1,1,3,3-tetramethylbutylperoxy-2-ethylhexanoate as a polymerization initiator was added dropwise over 2 hours. Then, the mixture was stirred at the same temperature for 1 hour, and 0.5 g of 1,1,3,3-tetramethylbutylperoxy-2-ethylhexanoate was added 5 times every hour to complete the polymerization reaction. Then, 235 g of xylene was added and dissolved to obtain a copolymer solution A-1. The viscosity of the obtained copolymer solution was 560 mPa·s (25°C), and the non-volatile content was 49.6%, and the Mw was 49,000.

[0051]

<Production Examples 2 to 8 (Production of solutions of copolymer A _A-2 to A-8)>

The organic solvents, reaction temperatures, monomers, and polymerization initiators shown in Table 1 were respectively used, and polymerization was performed by processes similar to those of Production Example 1, thereby obtaining copolymer solutions A-2 to A-8. The non-volatile content, the viscosity, and the weight average molecular weight of each copolymer solution obtained were measured. The results are shown in Table 1.

[0052]

<Production Examples 9 to 10 (Production of solutions of copolymers other than the copolymer A and the polymer B_E-1, E-2)>

The organic solvents, reaction temperatures, monomers, and polymerization initiators shown in Table 1 were respectively used, and polymerization was performed by processes similar to those of Production Example 1, thereby obtaining copolymer solutions E-1 to E-2. The non-volatile content, the viscosity, and the weight average molecular weight of each copolymer solution obtained were measured. The results are shown in Table 1.

[0053]

[Table 1]

Table 1	component	Production Example									
		1	2	3	4	5	6	7	8	9	10
		copolymer A									
monomer(a)	xylene	260	265	220	280	180	350	375	200	350	220
	triisopropylsilyl methacrylate	175	175	150	150	135	100	75	150	280	
monomer(b)	tri-2-ethylhexylsilyl methacrylate					20		10			
	triisopropylsilyl acrylate										175
	2-methoxyethyl acrylate	75		25	25	25	60	110	15	50	75
	2-ethoxyethyl acrylate								10		
	2-methoxyethyl methacrylate	25	100	200	200	165			150		25
	2-ethoxyethyl methacrylate								30		
	2-(2-ethoxyethoxy)ethyl acrylate								10		
	2-phenoxyethyl acrylate		15								
	glycidyl methacrylate		25								
	furfuryl acrylate			25							
	tetrahydrofurfuryl acrylate					15			5		
	tetrahydrofurfuryl methacrylate								5		
	methyl methacrylate	175	50	75	100	110	155	120	110	100	175
	ethyl acrylate						15				
	ethyl methacrylate						15				
	n-butyl acrylate	25	60	25	15	20	155	80	15	70	25
ratio of monomer (a) (mass%)	i-butyl methacrylate	25	75		10			75			25
	t-butyl methacrylate							15			
	cyclohexyl acrylate							15			
	styrene					10					
	ratio of monomer (a) (mass%)	35%	35%	30%	30%	31%	20%	17%	30%	56%	0%
	first added	3	2.5	2.5	16.5	2.5	3	2	2.3	3	4.5
	later added 5 times	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	amount of xylene added after completing the reaction	235	230	275	200	315	145	120	300	145	275
	reaction temperature [°C] (within ±5°C)	85	85	88	88	88	85	88	88	88	85
	non-volatile content [%]	49.6	49.8	50.1	50.4	49.7	49.9	49.8	49.6	49.6	50.1
physical properties of copolymer	weight average molecular weight [Mw]	49,000	53,000	49,000	23,000	59,000	48,000	47,000	51,000	51,000	53,000
	viscosity [mPa·s] (25°C)	560	350	570	300	710	380	400	720	300	350
copolymer solution		A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	E-1	E-2

<Production Examples 11 to 20 (Production of solutions of polymer B_B-1 to B-10)>

The organic solvents, reaction temperatures, monomers, and polymerization initiators shown in Table 2 were respectively used, and polymerization was performed by processes similar to those of Production Example 1,

thereby obtaining polymer solutions B-1 to B-10. The non-volatile content, the viscosity, and the weight average molecular weight of each polymer solution obtained were measured. The results are shown in Table 1.

[0054]

[Table 2]

Table 2

		Production Example															
		11	12	13	14	15	16	17	18	19	20	polymer B					
component		470	265	470	470	470	220	220	470	250	230						
monomer	xylene	125	115	10			225			100	100						
	2-methoxyethyl acrylate																
	2-ethoxyethyl acrylate																
	2-methoxyethyl methacrylate	25	10		25			125									
	2-ethoxyethyl methacrylate																
	2-(2-ethoxyethoxy)ethyl acrylate																
	2-phenoxyethyl acrylate					10											
	glycidyl methacrylate							25									
	furfuryl acrylate																
	tetrahydrofurfuryl acrylate																
	tetrahydrofurfuryl methacrylate																
	methyl methacrylate	125	200	200	125	100	275	140	200		5						
	ethyl acrylate			25													
	n-butyl acrylate	125	150	240	350	300			300	175	170						
	n-butyl methacrylate	50		25		40				10							
	i-butyl methacrylate	50	25							180	200						
	t-butyl methacrylate					25				10							
	cyclohexyl acrylate					25											
	cyclohexyl methacrylate							70									
	2-ethylhexyl acrylate							25									
	styrene							115									
polymerization initiator	first added	2.5	7.5	2.5	2.5	2.5	14	20	2.5	2	1.9						
	later added 5 times	0.5	0.5	0.5	0.5	0.5	0.2	0.2	0.5	3.5	0.2						
amount of xylene added after completing the reaction		25	58	25	25	25	265	260	25	250	270						
reaction temperature [°C] (within ±5°C)		88	88	88	88	88	85	85	88	125	88						
copolymer physical properties	non-volatile content [%]	49.9	59.7	50.0	49.7	50.1	49.8	50.2	49.6	49.8	50.4						
	weight average molecular weight [Mw]	44,000	32,000	43,000	44,000	41,000	36,000	21,000	43,000	27,000	51,000						
	viscosity [mPa·s] (25°C)	350	430	600	270	300	720	360	420	120	270						
polymer solution		B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9	B-10						

[0055]

<Production Example 21(Production of dispersion stabilizer (shell component))>

To a flask equipped with a thermometer, reflux condenser, stirrer, and dropping funnel, 450 g of mineral spirit was charged and heated to 95 to 105°C under nitrogen atmosphere. With agitation, a mixed solution of 500 g of n-butyl methacrylate, 500g of 2-ethylhexyl acrylate, and 3 g of t-butylperoxyoctoate as a polymerization initiator was added dropwise over 3 hours while keeping the temperature at 95 to 105°C. After dropping, 2.5 g of t-butylperoxyoctoate was added twice every 30 minutes, while keeping the temperature at 95 to 105°C. Then the mixture was further stirred for 2 hours and then diluted with 550 g of mineral spirit to obtain a dispersion stabilizer. The viscosity of the obtained polymer solution was 660 mPa·s (25°C), and the non-volatile content was 50.2%, and the Mw was 76,000.

[0056]

<Production Example 22(Production of a solution of polymer B by non-aqueous dispersion polymerization_B-9)>

To a flask equipped with a thermometer, reflux condenser, stirrer, and dropping funnel, 133.4 g of a dispersion stabilizer (produced in Production Example 21) was charged and heated to 100 to 110°C under nitrogen atmosphere. With agitation, a mixed solution of 16 g of methyl methacrylate, 7.2 g of ethyl acrylate, 10.2 g of methacrylic acid, and 0.8 g of Nyper BMT-K40 (40% xylene solution of benzoyl/m-toluoyl peroxide, available from NOF CORPORATION) as a polymerization initiator was added dropwise while keeping the temperature at 100 to 110°C over 3 hours. After dropping, 0.2 g of Nyper BMT-K40 was added twice every 30 minutes while keeping the temperature at 100 to 110°C. Then the mixture was further stirred for 2 hours and then diluted with 32 g of mineral spirit to obtain B-9. The viscosity of the obtained polymer solution was 980 mPa·s (25°C), and the non-volatile content was 50.4%, and the Mw was 68,000.

[0057]

<Production Example 23(Production of a solution of a copolymer other than the copolymer A and the polymer B_E-3)>

To a flask equipped with a thermometer, reflux condenser, stirrer, and dropping funnel, 500 g of xylene was charged and heated to 125 to 130°C under a nitrogen atmosphere. With agitation, a mixed solution of 50 g of methyl methacrylate, 120 g of n-butyl acrylate, 330 g of 2-methoxyethyl acrylate, 15 g of t-butylperoxyoctoate, which is a polymerization initiator, and 1 g of NOFMER MSD (available from NOF CORPORATION), which is a chain transfer agent, was added dropwise while keeping the temperature at 125 to 130°C. After dropping, 1 g of t-butylperoxyoctoate was added 3 times every hour while keeping the temperature at 125 to 130°C, and the mixture was further stirred for 2 hours to obtain E-3. The viscosity of the obtained copolymer solution was 60 mPa·s (25°C), and the non-volatile content was 52.4%, and the Mw was 9,500.

[0058]

<Production Example 24 (Production of rosin zinc salt solution)>

To a flask equipped with a thermometer, a reflux condenser, and a stirrer, 240 g of Chinese gum rosin (WW) and 360 g of xylene were charged, and furthermore, 120 g of zinc oxide was added so that all the resin acids in the said rosin formed zinc salts, and the mixture was refluxed and dehydrated under reduced pressure at 70-80°C for 3 hours. The mixture was then cooled and filtered to obtain a xylene solution of rosin zinc salts (dark brown transparent liquid, 50% solids). The non-volatile content of the solution obtained was 50.4%.

[0059]

<Production Example 25 (Production of trimethyl isobutenylcyclohexene carboxylic acid solution)>

To a flask equipped with a thermometer, a reflux condenser, and a stirrer, 320 g of alloocimene, 175 g of methacrylic acid, and 0.17 g of MEHQ were charged, heated, and stirred at 35 to 45°C for 24 hours. Then, the unreacted raw materials were distilled off under reduced pressure to obtain 73 g of brown viscous trimethyl isobutenylcyclohexene carboxylic acid. This was added with xylene, and a trimethyl isobutenylcyclohexene carboxylic acid solution (solid content 50%) was obtained.

[0060]

<Examples 1 to 44 and Comparative Examples 1 to 8 (Production of coating compositions)>

Coating compositions were prepared by mixing the components shown in Tables 3 to 9 in the ratio (mass%) shown in these Tables and mixing and dispersing the components with glass beads having a diameter of 1.5 to 2.5 mm.

Table 3

component		Example							
		1	2	3	4	5	6	7	8
copolymer A	A-1	12	12	12	12	12	12	12	12
polymer B	B-1	12	12	12	12	12	12	12	12
plasticizer C	chlorinated paraffin	1							
	E-2000H		1						
	Lutonal A-25			1					
	DINP				1				
	DINCH					1			
	DEHT						1		
	TOTM							1	
	ATBC								1
antifouling agent	cuprous oxide	45	45	45	45	45	45	45	45
	copper pyrrithione	3	3	3	3	3	3	3	3
elution regulator	SeaNine	1	1	1	1	1	1	1	1
	rosin solution	3	3	3	3	3	3	3	3
	rosin zinc salt solution	3	3	3	3	3	3	3	3
other additives (pigment)	red oxide	2	2	2	2	2	2	2	2
	talc	2	2	2	2	2	2	2	2
	zinc oxide	4	4	4	4	4	4	4	4
	titanium oxide	1	1	1	1	1	1	1	1
	tetraethoxysilane	1	1	1	1	1	1	1	1
other additives (dehydrating agent, antisag agent)	aliphatic amide thixotropic agent	3	3	3	3	3	3	3	3
solvent	xylene	7	7	7	7	7	7	7	7
sum		100	100	100	100	100	100	100	100
Test Example 1 ($\mu\text{m}/\text{month}$)	0 - 6 months later	4.2	4.9	3.2	4.7	5.2	5.1	4.8	5.1
	6 - 12 months later	4.5	5.1	4.1	4.5	5.7	5.5	5.1	4.9
	12 - 18 months later	4.1	4.5	3.8	4.1	5.6	5.3	5.3	4.7
	18 - 24 months later	4.6	5.2	4.1	4.5	5.1	5.3	5.2	5.0
Test Example 2 conditions of coating film	12 months later	A	A	B	A	B	A	A	B
	24 months later	A	A	C	B	B	B	A	C

Table 4

component		Comparative Example							
		1	2	3	4	5	6	7	8
copolymer A	A-1	12	24						12
polymer B	B-1	12		24	12		12		
other copolymer	E-1				12	24			
	E-2						12	24	
	E-3								12
plasticizer C	chlorinated paraffin		1	1	1	1	1	1	1
antifouling agent	cuprous oxide	45	45	45	45	45	45	45	45
	copper pyrithione	3	3	3	3	3	3	3	3
	SeaNine	1	1	1	1	1	1	1	1
elution regulator	rosin solution	3	3	3	3	3	3	3	3
	rosin zinc salt solution	3	3	3	3	3	3	3	3
	red oxide	2	2	2	2	2	2	2	2
other additives (pigment)	talc	2	2	2	2	2	2	2	2
	zinc oxide	4	4	4	4	4	4	4	4
	titanium oxide	1	1	1	1	1	1	1	1
other additives (dehydrating agent, antisag agent)	tetraethoxysilane	1	1	1	1	1	1	1	1
	aliphatic amide	3	3	3	3	3	3	3	3
	thixotropic agent								
solvent	xylene	7	7	7	7	7	7	7	7
sum		99	100	100	100	100	100	100	100
Test Example 1 (μm/month)	0 - 6 months later	1.1	1.6	0.8	1.2	1.7	3.7	1.8	5.1
	6 - 12 months later	0.4	0.7	0.2	0.4	1.1	5.4	5.7	4.9
	12 - 18 months later	0.2	0.5	0.3	0.7	0.8	8.2	9.9	peeling
	18 - 24 months later	0.2	0.7	0.3	0.6	0.4	15.7	17.8	—
Test Example 2 conditions of coating film	12 months later	C	C	D	C	C	D	D	E
	24 months later	D	D	E	D	D	D	E	E

[0063]

[Table 5]

Table 5

component		Example					
		9	10	11	12	13	14
copolymer A	A-2	12					
	A-3		12				
	A-4			12			
	A-5				12		
	A-6					12	
	A-7						12
polymer B	B-1	12	12	12	12	12	12
plasticizer C	chlorinated paraffin	1	1	1	1	1	1
antifouling agent	cuprous oxide	45	45	45	45	45	45
	copper pyrithione	3	3	3	3	3	3
	SeaNine	1	1	1	1	1	1
elution regulator	rosin solution	3	3	3	3	3	3
	rosin zinc salt solution	3	3	3	3	3	3
other additives (pigment)	red oxide	2	2	2	2	2	2
	talc	2	2	2	2	2	2
	zinc oxide	4	4	4	4	4	4
	titanium oxide	1	1	1	1	1	1
other additives (dehydrating agent, antisag agent)	tetraethoxysilane	1	1	1	1	1	1
	aliphatic amide thixotropic agent	3	3	3	3	3	3
solvent	xylene	7	7	7	7	7	7
sum		100	100	100	100	100	100
Test Example 1 ($\mu\text{m}/\text{month}$)	0 - 6 months later	4.0	5.2	3.9	4.7	3.7	4.1
	6 - 12 months later	4.1	4.9	3.7	5.1	3.8	4.0
	12 - 18 months later	4.3	5.6	3.8	5.0	4.0	4.0
	18 - 24 months later	4.2	5.2	3.9	4.9	4.1	4.3
Test Example 2 conditions of coating film	12 months later	A	A	A	A	A	A
	24 months later	A	B	B	A	A	B

Table 6

component		Example									
		15	16	17	18	19	20	21	22		
copolymer A	A-1	12	12	12	12	12	12	12	12		
	B-2	10									
	B-3		12								
	B-4			12							
	B-5				12						
	B-6					12					
	B-7						12				
	B-8							12			
	B-9								12		
plasticizer C	chlorinated paraffin	1	1	1	1	1	1	1	1	1	1
	cuprous oxide	45	45	45	45	45	45	45	45	45	45
	copper pyrrhione	3	3	3	3	3	3	3	3	3	3
antifouling agent	SeaNine	1	1	1	1	1	1	1	1	1	1
	rosin solution	3	3	3	3	3	3	3	3	3	3
	rosin zinc salt solution	3	3	3	3	3	3	3	3	3	3
elution regulator	red oxide	2	2	2	2	2	2	2	2	2	2
	talc	2	2	2	2	2	2	2	2	2	2
	zinc oxide	4	4	4	4	4	4	4	4	4	4
	titanium oxide	1	1	1	1	1	1	1	1	1	1
other additives (pigment)	tetraethoxysilane	1	1	1	1	1	1	1	1	1	1
	aliphatic amide	3	3	3	3	3	3	3	3	3	3
	thixotropic agent										
solvent	xylene	9	7	7	7	7	7	7	7	7	7
	sum	100	100	100	100	100	100	100	100	100	100
Test Example 1 (μm/month)	0 - 6 months later	5.1	4.7	3.9	4.5	4.2	5.4	4.8	5.3		
	6 - 12 months later	5.3	4.9	4.1	4.4	4.1	5.7	2.3	4.5		
	12 - 18 months later	5.7	5.1	3.8	4.2	4.5	5.3	2.0	2.5		
	18 - 24 months later	5.5	4.8	3.9	4.4	4.6	5.5	2.2	2.1		
Test Example 2 conditions of coating film	12 months later	A	A	A	A	A	A	A	A	B	B
	24 months later	A	A	A	B	A	A	B	B	B	B

[0065]

[Table 7]

Table 7

component		Example								
		23	24	25	26	27	28	29	30	31
copolymer A	A-1	15	12.4		7	5	20	15	10.5	7.5
	A-2			14						
	A-3					5				
	A-4			3						
	A-5				3					
polymer B	B-1	15	10				10	15	2.5	2.5
	B-2			4						
	B-3		2.4		3					
	B-4					4				
	B-5				2				1	4
plasticizer C	chlorinated paraffin	1	0.5				1	1	1	1
	Toyo ParaxA50			0.5	0.5	1				
	E-2000H			0.5	0.5					
	Lutonal A25					0.5				
	DINP				0.5					
	DINCH		0.5		0.5				0.5	0.5
	DEHT				0.5				0.5	0.5
	TOTM				0.5				0.5	0.5
antifouling agent	ATBC					0.5				
	cuprous oxide	45	40	40	40	45	45	30	30	30
	rhodan copper		5		1					
	copper pyrithione	3	2	1	2	2	3	1.5	1.5	1.5
	zinc pyrithione			1						
	Zineb			5	1					
	SeaNine	1	1	1	1	1	1	1	1	1
	Econea				1				0.5	
elution regulator	medetomidine				0.5					0.5
	rosin solution				5				2	2
	rosin zinc salt solution		6.2	10	5				10	10
	hydrogenated rosin solution				5	8.5			2	2
	NT-RMZ				5	8.5				
other additives (pigment)	red oxide	2	2	2	2	2	2	2	2	2
	talc	2	2	2	3	3	2	7	7	7
	zinc oxide	4	4	4	2	2	4	14	14	14
	titanium oxide	1	1	1	1	1	1	1	1	1
other additives (dehydrating agent, antisag agent)	tetraethoxysilane	1	0.5	1	0.5	0.5	1	0.5	0.5	0.5
	anhydrous gypsum		0.5		0.5					
	aliphatic amide thixotropic agent	3	4	4	3	3	3	2	2	2
solvent	xylene	7	6	6	4	7.5	7	10	10	10
sum		100	100	100	100.5	100	100	100	100	100
Test Example 1 (μm/month)	0 - 6 months later	4.2	5.1	5.1	5.5	5.1	4.7	2.9	6.1	5.4
	6 - 12 months later	4.5	5.2	5.2	5.2	5.0	4.5	3.4	5.9	4.8
	12 - 18 months later	4.7	5.3	5.4	5.4	4.9	3.5	3.6	6.2	5.1
	18 - 24 months later	4.6	5.7	5.1	5.4	5.2	3.1	3.5	6.4	5.2
Test Example 2 conditions of coating film	12 months later	A	A	B	A	A	A	A	A	A
	24 months later	A	A	B	A	B	B	A	B	B

[0066]

[Table 8]

Table 8

component		Example						
		32	33	34	35	36	37	38
copolymer A	A-1	4.5	4.5		1		12	
	A-2		0.5					
	A-3							13
	A-4		5					
	A-5		5					
	A-6			15				
polymer B	A-7		3.7	3.7		4		
	B-1	2.5			7		12	13
	B-5	6						
	B-6		1.5	1.5		2		
	B-7		1.5	1.5		1		
plasticizer C	B-8	1				1		
	chlorinated paraffin	1		0.5	0.5	0.5	0.5	0.5
	Toyo ParaxA50						0.5	0.5
	E-2000H			0.5	0.5	0.5		
	Lutonal A25		0.5					
	DINP		0.5					
	DINCH	0.5			2.5	2.5	0.5	0.5
	DEHT	0.5						
antifouling agent	TOTM	0.5						
	ATBC		0.5	0.5	0.5	0.5		
	cuprous oxide	30	30	30	30	30	45	
	copper pyrithione	1.5	1.5	1.5	1.5	1.5	2	
	zinc pyrithione						1	2.5
	Zineb							
	SeaNine	1	1	1	1	1	1	1
elution regulator	Econea							7
	medetomidine							0.5
	rosin solution						3	
	rosin zinc salt solution	14	9.3	9.3				3
	hydrogenated rosin solution				19	19		
	NT-RMZ							14
other additives (pigment)	trimethyl isobutenylcyclohexene carboxylic acid						3	3
	red oxide	2	2	2	2	2	2	2
	talc	7	7	7	7	7	2	5
	zinc oxide	14	14	14	14	14	4	15
other additives (dehydrating agent, antisag agent)	titanium oxide	1	1	1	1	1	1	1
	tetraethoxysilane	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	anhydrous gypsum						0.5	0.5
	aliphatic amide thixotropic agent	2	3	3	4	4	3	3
solvent	xylene	10.5	7.5	7.5	8	8	6	14
	denatured alcohol						0.5	0.5
sum		100	100	100	100	100	100	100
Test Example 1 ($\mu\text{m}/\text{month}$)	0 - 6 months later	4.5	4.7	5.1	3.9	4.2	4.8	2.8
	6 - 12 months later	4.7	4.7	4.9	3.6	3.9	4.5	2.5
	12 - 18 months later	4.6	5.2	4.8	3.7	3.8	5.2	3.1
	18 - 24 months later	4.5	4.9	4.7	3.6	3.7	5.7	2.7
Test Example 2 conditions of coating film	12 months later	A	B	A	A	A	A	A
	24 months later	A	C	A	B	B	B	B

[0067]

[Table 9]

Table 9

component		Example					
		39	40	41	42	43	44
copolymer A	A-1					5	7
	A-3	13	13			2	
	A-4						1.5
	A-8				12	2	2
polymer B	B-1	13	13	13	12		1.5
	B-9					3	1
	B-10					3	1
plasticizer C	chlorinated paraffin	0.5	0.5		1	0.5	
	Toyo ParaxA50	0.5	0.5				
	E-2000H			0.5			
	Lutonal A25			0.5			
	DINP			0.5		0.5	0.5
	DINCH	0.5	0.5	0.5		0.5	0.5
	DEHT			0.5			
	TOTM					0.5	0.5
antifouling agent	ATBC			0.5		0.5	0.5
	cuprous oxide				45	30	30
	copper pyrithione				3	1	1
	zinc pyrithione	2.5	2.5	2			
	Zineb			0.5			0.5
	SeaNine	1	1	1	1	0.5	0.5
	Econea	7	7	7			0.5
elution regulator	medetomidine	0.5	0.5	0.5		0.5	0.5
	rosin solution						2
	rosin zinc salt solution		17	12	3	12	8
	hydrogenated rosin solution				2	1	1
	NT-RMZ	20		5	1	1	1
	trimethyl isobutenylcyclohexene carboxylic acid		3	3			2
other additives (pigment)	red oxide	2	2	2	2	2	2
	talc	5	5	5	2	7	7
	zinc oxide	15	15	15	4	14	14
	titanium oxide	1	1	1	1	1	1
other additives (dehydrating agent, antisag agent)	tetraethoxysilane	0.5	0.5	0.5	1	0.5	1
	anhydrous gypsum	0.5	0.5	0.5			
	aliphatic amide thixotropic agent	3	3	3	3	2	2
solvent	xylene	14.5	14.5	13	7	10	9.5
	denatured alcohol						0.5
sum		100	100	87	100	100	100
Test Example 1 (μm/month)	0 - 6 months later	2.5	2.4	1.8	5.4	3.7	4.5
	6 - 12 months later	2.4	1.2	1.4	5.7	4.1	5.1
	12 - 18 months later	2.7	1.1	1.2	6.1	4.7	5.0
	18 - 24 months later	1.9	1.6	1.5	5.9	5.1	5.5
Test Example 2 conditions of coating film	12 months later	A	A	B	B	B	B
	24 months later	A	A	B	B	B	B

[0068]

The following tests were conducted on the coating compositions of Examples and Comparative Examples.

[0069]

<Test Example 1 (Rotary test)>

A rotating drum with a diameter of 515 mm and a height of 440 mm was attached to the center of the water tank so that it could be rotated by a motor. Further, a cooling device for keeping the temperature of seawater constant and a pH automatic controller for keeping the pH of seawater constant were attached.

A test plate was prepared according to the following method.

First, a rust preventive coating (epoxy vinyl A/C) was applied on a titanium plate (71×100×0.5 mm) and dried to form a rust preventive coating film so that the thickness of the film after drying is about 100 μm . Then, each of the coating compositions obtained in Examples and Comparative Examples was applied on the rust preventive coating film so that the thickness after drying was about 500 μm . The obtained coated product was dried at 40°C for 3 days to prepare a test plate having a dry coating film with a thickness of about 500 μm .

One of the prepared test plates was fixed to the rotating drum of the rotating device of the above device so that it came into contact with seawater, and the rotating drum was rotated at a speed of 20 knots. During rotating, the temperature of seawater was kept at 15°C and the pH was kept at 8.0 to 8.2, and the seawater was replaced every week.

The amount of coating film dissolved was calculated by measuring the initial film thickness and the remaining film thickness after every 6 months of each test plate with a laser focus displacement meter and calculating the thickness of the coating film dissolved from the difference. The amount of coating film dissolved was represented by the amount of coating film dissolved per month ($\mu\text{m}/\text{month}$).

[0070]

<Test Example 2 (Physical property test of coating film)>

Twelve and twenty-four months after carrying out the rotary test, the test plates were dried, and the surface of each coating film was visually observed to evaluate the condition of the coating film. The evaluation was performed by the following method.

[0071]

A: No defects were observed.

B: Hairline cracks were observed in less than 10% of the total surface area of the coating film.

C: Hairline cracks were observed in 10 to 30% of the total surface area of the coating film.

D: Hairline cracks were observed in more than 30% of the total surface area of the coating film.

E: Coating film defects such as large cracks, blisters, peelings (only the surface of the coating film or a part of the edges of the coating film are peeled off), or peelings (the entire coating film is peeled off, and the test coating film does not remain) were observed.

[0072]

<Test results>

From Test Examples 1 and 2, it was revealed that the antifouling coating film containing the three components of the copolymer A, the polymer B, and the plasticizer C exhibits a good film dissolution in seawater

at 15°C for 24 months without causing coating film defects (Example 1). When any of the three essential components of the present invention were lacking, this effect was lost and the amount of the film dissolution decreased, and coating film defects such as large cracks and peelings occurred after 24 months (Comparative Examples 1-3).

Further, It was found that, when the ratio of the triorganosilyl monomer component in the copolymer A exceeds the range of the present invention, even if the structure is similar to that of the copolymer A, the dissolution property is remarkably reduced (Comparative Examples 4 and 5). In addition, when triorganosilyl acrylate is used as a substitute for the triorganosilyl methacrylate, even if the ratio of the triorganosilyl monomer component in the copolymer A is within the range of the present invention, the coating composition dissolves but does not have a stable dissolution property or crack resistance (Comparative examples 6, 7).

Further, when a copolymer having a small Mw is used as a substitute for the polymer B, even if the copolymer is a (meth)acrylate ester copolymer similar to the polymer B, a defect that the antifouling coating film peels off occurs (Comparative example 8).

Within the scope of the present invention, various monomer compositions can be applied to the copolymer A and the polymer B (Tables 5 and 6), and it can be seen that various plasticizers can be used (Table 3).

Further, it was found that when the copolymer A, the polymer B, and the plasticizer are contained in appropriate amounts, the present effect can be exhibited even if the compounding amount and kind of the antifouling agent, the pigment component, the solute regulator component and the like are changed (Tables 7 to 9).

[0073]

Details of each component in Tables 3 to 9 are as follows.

[0074]

<Plasticizer>

chlorinated paraffin: product name "Paraffin Chlorinated" (Cl: 40%) (available from Wako Pure Chemical Industries, Ltd.)

Toyo Parax A50: product name "Toyo Parax A50" (available from Tosoh Corporation)

E-2000H: epoxidized soybean oil: product name "Sansozizer E-2000H" (available from New Japan Chemical Co., Ltd.)

LutonalA25: product name "Lutonal(registered tradename) A25" (available from BASF)

DINP: diisononyl phthalate: product name "Diisononyl Phthalate" (available from Wako Pure Chemical Industries, Ltd.)

DINCH: diisononyl 1,2-cyclohexane dicarboxylate: product name "HEXAMOLL (registered tradename) DINCH (registered tradename)" (available from BASF)

DEHT: di-2-ethylhexyl terephthalate: product name "Bis(2-ethylhexyl) terephthalate" (available from SIGMA-ALDRICH, INC.)

TOTM: tri-2-ethylhexyl trimellitate: product name "Tris(2-ethylhexyl) Trimellitate" (available from TOKYO CHEMICAL INDUSTRY CO., LTD.)

ATBC: acetyl tributyl citrate: product name "Tributyl O-Acetylcitrate" (available from TOKYO CHEMICAL INDUSTRY CO., LTD.)

[0075]

<Antifouling agent>

cuprous oxide: product name "NC-301" (available from NISSIN CHEMCO LTD.)

rhodan copper: product name "Copper (I) thiocyanate" (available from Sigma-Aldrich, Inc.)

copper pyrithione: product name "copper Omadine" (available from Arch Chemical, Inc.)

zinc pyrithione: product name "zinc Omadine" (available from Arch Chemical, Inc.)

Zineb: product name "Zineb" (available from Sigma-Aldrich, Inc.)

Sea Nine: product name "Sea Nine 211", 4,5-dichloro-2-n-octyl-3(2H)isothiazoline (30% solids xylene solution, available from Rohm & Haas, Inc.)

Econia: product name "Econea 028" 2-(p-chlorophenyl)3-cyano-4-bromo-5-trifluoromethyl pyrrole, (available from JANSSEN PMP)

medetomidine: product name "4-(1-(2,3-Dimethylphenyl) ethyl)-1H-imidazole" (available from Wako Pure Chemical Industries, Ltd.)

[0076]

<Elution regulator>

rosin zinc salt solution: The one produced in Production Example 24 was used.

hydrogenated rosin solution: xylene solution (50% solids) of product name "HYPALE CH" (available from ARAKAWA CHEMICAL INDUSTRIES, LTD.)

rosin solution: xylene solution (50% solids) of Chinese gum rosin (WW)

NT-RMZ: hydrogenated rosin zinc salt solution: product name "NT-RMZ", 65% solids (available from Nitto Kasei Co., Ltd.)

trimethyl isobutenyl cyclohexene carboxylic acid solution: The one produced in Production Example 25.

[0077]

<Other additives, solvents>

red oxide: product name "TODA COLOR EP-13D" (available from Toda Pigment Corp.)

talc: product name "CROWN TALC 3S" (available from matsumura sangyo Co., Ltd.)

zinc oxide: product name "zinc oxide II" (available from Seido Chemical Industry Co., Ltd.)

titanium oxide: product name "FR-41" (available from FURUKAWA CO., LTD.)

tetraethoxysilane: product name "Tetraethyl Orthosilicate" (available from TOKYO CHEMICAL INDUSTRY CO., LTD.)

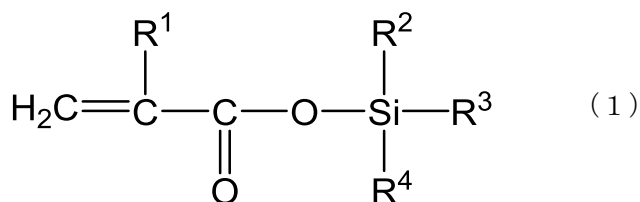
anhydrous gypsum: product name "D-1" (NORITAKE CO., LIMITED)

aliphatic amide thixotropic agent: product name "Disparlon A603-20X" (available from Kusumoto Chemicals, Ltd.)

denatured alcohol: product name "Clean Ace High" (IMAZU CHEMICAL CO.LTD)

CLAIMS

1. An antifouling coating composition, comprising:
a copolymer A;
a polymer B, which is not a (meth)acrylate silyl ester copolymer; and
a plasticizer C; wherein:
the copolymer A is a copolymer of a monomer (a) and an ethylenically unsaturated monomer (b) other than the monomer (a);
the monomer (a) is represented by general formula (1);
[chemical formula 1]



in the general formula, R¹ is a methyl group, and R² to R⁴ are the same or different and each represents a C3-C8 branched alkyl group or a phenyl group;

content of the monomer (a) is 15 to 35mass% with respect to a total mass of the monomer (a) and the monomer (b);

the polymer B is a (meth)acrylate ester polymer other than the copolymer A and has a weight average molecular weight of 20,000 to 100,000.

- 2 The antifouling coating composition according to claim 1, wherein the plasticizer C contains chlorinated paraffin.